

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23C 16/18, C07F 15/00	A1	(11) International Publication Number: WO 99/24635 (43) International Publication Date: 20 May 1999 (20.05.99)
(21) International Application Number: PCT/US98/23791 (22) International Filing Date: 10 November 1998 (10.11.98) (30) Priority Data: 08/966,797 10 November 1997 (10.11.97) US (71) Applicant: ADVANCED TECHNOLOGY MATERIALS, INC. [US/US]; 7 Commerce Drive, Danbury, CT 06810 (US). (72) Inventors: BAUM, Thomas, H.; 2 Handol Lane, New Fairfield, CT 06776 (US). XU, Chong-ying; 6 Canterbury Arms, 190 Wellsville Avenue, New Milford, CT 06776 (US). (74) Agent: HULTQUIST, Steven, J.; Intellectual Property/Technology Law, P.O. Box 14329, Research Triangle Park, NC 27709 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>With amended claims and statement.</i>
(54) Title: METHOD OF FABRICATING IRIIDIUM-BASED MATERIALS AND STRUCTURES ON SUBSTRATES, AND IRIIDIUM SOURCE REAGENTS THEREFOR (57) Abstract A method of forming an iridium-containing film on a substrate, from an iridium-containing precursor thereof which is decomposable to deposit iridium on the substrate, by decomposing the precursor and depositing iridium on the substrate in an oxidizing ambient environment which may for example contain an oxidizing gas such as oxygen, ozone, air, and nitrogen oxide. Useful precursors include Lewis base stabilized Ir(I) β -diketonates and Lewis base stabilized Ir(I) β -ketoiminates. The iridium deposited on the substrate may then be etched for patterning an electrode, followed by depositing on the electrode a dielectric or ferroelectric material, for fabrication of thin film capacitor semiconductor devices such as DRAMs, FeRAMs, hybrid systems, smart cards and communication systems.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**METHOD OF FABRICATING IRIIDIUM-BASED MATERIALS
AND STRUCTURES ON SUBSTRATES, AND IRIIDIUM
SOURCE REAGENTS THEREFOR**

5

DESCRIPTION

Field Of The Invention

10 This invention relates to a method of forming iridium- or iridium-containing materials on substrates, such as Ir-based electrode structures for microelectronic devices and subassemblies, as well as to Ir source reagent materials, and novel dielectric capacitor or ferroelectric material structures.

15 **Description of the Related Art**

Iridium (Ir) and iridium oxide (IrO_2) are of great interest for use as electrode materials in both dynamic random access memories (DRAMs) and for ferroelectric-based memory devices (FRAMs) which incorporate perovskite metal
20 oxide thin-films as the capacitor layer.

The advantages of Ir over other possible electrode materials include ease of deposition, the ability to "dry etch" the material, the ability to form a stable conducting oxide at high temperatures in an oxidizing environment, and the ability
25 to operate stably at high temperatures in a working device.

The deposition and processing of Ir-based electrodes is highly desirable in view of the aforementioned advantages. Further, the formation of IrO_2 acts as a diffusion barrier to oxidation of conducting polysilicon vias or plugs, as is required in high density DRAM or FRAM devices.

5

Based on the need for Ir-based electrodes, the art has continued to seek improvements in source materials and deposition techniques for the formation of Ir-based films.

- 10 The art has variously disclosed the chemical vapor deposition of iridium for the manufacture of electronic devices in a reducing atmosphere, such as hydrogen gas environment. The art has taught the use of such reducing atmosphere for the purpose of achieving the deposition of element metal iridium for electrodes in applications in which high temperature dielectric materials (e.g., SBT, BST, PZT, 15 PLZT, PNZT, LaCaMnO_3 , etc., wherein SBT = strontium bismuth tantalate, BST = barium strontium titanate, PZT = lead zirconium titanate, PLZT = lead lanthanum zirconium titanate, PNZT = lead niobium zirconium titanate) are deposited on the electrode, to minimize the possibility of degradation of the dielectric in such applications and to concurrently achieve the formation of high purity metal.

20

The art has especially sought improvements in process technology for the formation of semiconductor and ferroelectric structures which employ Ir electrodes specifically associated with complex dielectric or ferroelectric material layers as thin-film capacitors.

25

It is an object of the present invention to provide novel source reagents and a process for the formation of iridium-based electrodes that achieve a material

simplification in fabrication efficiency and cost, and provide an electrode structure that is highly advantageous for integration with silicon device technology, being efficient and readily fabricated.

- 5 It is another object of the invention to provide a simplified method for the fabrication of metal oxide thin film capacitor structures including iridium, iridium oxide or iridium-containing electrode elements, as metal contacts for the oxide DRAM and FRAM devices.
- 10 Other objects and advantages of the present invention will be more fully apparent from the ensuing disclosure and appended claims.

SUMMARY OF THE INVENTION

15

This invention relates to a method of forming iridium- or iridium-containing materials on substrates, such as Ir-based electrode structures for microelectronic devices and subassemblies, and catalytic materials, as well as to Ir source reagent materials, and novel dielectric material structures.

20

As used herein, the term "Ir-based" or "iridium-based" refers broadly to elemental iridium, iridium oxide and iridium-containing material compositions.

The present invention also relates to novel high temperature dielectric or
25 ferroelectric thin film capacitor structures including Ir-based electrode elements.

In one aspect, the invention relates to a method of forming an iridium-containing film on a substrate, from an iridium-containing precursor thereof which is decomposed to deposit iridium on the substrate, such method comprising decomposing the precursor and depositing iridium on the substrate in an oxidizing ambient environment. The deposition of iridium on the substrate may be carried out in any suitable manner and by any appropriate techniques of the art, including chemical vapor deposition (CVD), assisted CVD, or physical deposition methods such as ion plating, rapid thermal processing, molecular beam epitaxy, etc.

10 As used herein, the term "oxidizing ambient environment" means an environment including oxygen-containing gas, such as oxygen, ozone, air, nitrogen oxide (NO_x), or the like. Such oxidizing atmosphere may be provided in a deposition chamber or reaction vessel in which the deposition is carried out, and enables the formation of iridium or iridium oxide on the substrate. Accordingly, the deposition may be conducted in an ambient air environment, thereby simplifying the formation of the iridium-containing film on the substrate. In an alternate embodiment, IrO_2 may be formed in a post-deposition process from Ir metal by treatment in an oxidizing environment.

20 The Ir precursor material may be of any suitable composition and type. In preferred practice of the present invention, the precursor may suitably comprise a Lewis base-stabilized β -diketonate iridium composition or a Lewis base-stabilized beta-ketoiminate composition, as hereafter more fully described.

25 When the iridium-containing film is employed to form an electrode or other patterned structure on the substrate, the deposited iridium or iridium oxide film may be dry etched with a halogen-based plasma and/or preferably, XeF_2 , as more

fully described in U.S. Patent Application No. 08/966,796 filed November 10, 1997 in the names of Thomas H. Baum and Frank Dimeo, Jr. for "Iridium-Based Electrode Structures, and Method of Making the Same," the disclosure of which hereby is incorporated herein in its entirety. In such dry etching of a deposited
5 iridium or iridium oxide film, the etch rates can optionally be enhanced through the use of Lewis-based adducts or electron back-bonding species such as carbon monoxide, trifluorophosphine, or trialkylphosphines.

In yet another aspect of the present invention, the iridium-containing film
10 subsequent to its formation as an electrode structure may have deposited thereon a high temperature dielectric and/or ferroelectric material. An oxidizing ambient environment may be employed for the deposition of the iridium-containing film or may be used solely during the deposition of the oxide dielectric/ferroelectric.

15 It may therefore be unnecessary to purge the chamber of a reducing atmosphere, or to transfer the substrate article bearing the iridium-containing film from the iridium deposition chamber to a dielectric/ferroelectric deposition chamber, as has been done in the prior art to accommodate the usage of hydrogen or other reducing gas (forming gas) atmospheres in the iridium electrode formation step.

20

The method of this invention therefore achieves a substantial simplification of the procedure for forming a capacitor or other microelectronic device in which the iridium-containing electrode is overcoated with a dielectric or ferroelectric material.

25

Another aspect of the invention relates to a microelectronic device structure comprising an iridium oxide electrode element overcoated by a high temperature

dielectric, e.g., SBT, PZT, BST, PLZT, PNZT, LaCaMnO₃, etc., wherein the electrode is conductively operative in relation to the high temperature dielectric. As used herein, high temperature dielectric refers to a dielectric material deposited on the electrode at a temperature above about 300°C. By way of example, 5 dielectric films of lead zirconium titanate (PZT) are typically deposited at temperatures on the order of 500-600°C.

Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

10

DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED EMBODIMENTS THEREOF

15 The present invention relates to the discovery that Ir-based electrode structures can be readily formed without the necessity of depositing the Ir component from a precursor or source material in a reducing atmosphere, as has heretofore been the approach and objective of the prior art.

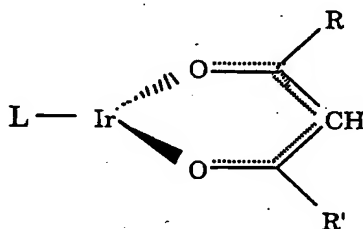
20 Contrariwise, the present invention contemplates a method of forming an iridium-containing film on a substrate, from an iridium-containing precursor thereof which is decomposed to deposit iridium on the substrate, in which the decomposition of the precursor and the deposition of iridium on the substrate is carried out in an oxidizing ambient environment to deposit iridium in the form of iridium *per se* or 25 in the form of iridium oxide.

Iridium may be deposited on the substrate in the method of the present invention in any suitable manner, including chemical vapor deposition, liquid delivery,

sputtering, ablation, or any other suitable technique known in the art for deposition of metal on a substrate from a metal-organic or other precursor or source material. Among the foregoing, chemical vapor deposition is preferred when the iridium-based structures being formed have critical dimensions below about 0.5 microns.

In the method of the invention, the precursor for the iridium component may be any suitable iridium precursor compound, complex or composition which is advantageous for yielding iridium for deposition on the substrate. The iridium precursor may for example comprise a Lewis base-stabilized β -diketonate iridium composition or a Lewis base-stabilized β -ketoiminate composition, of the formulae:

Lewis base stabilized Ir(I) β -diketonates of formula I:

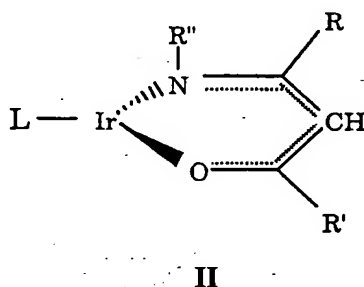


I

wherein R and R' are the same or different and may be H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base, preferably alkene, diene, cycloalkene, cycloalkadiene, cyclooctatetraene, alkyne, substituted alkyne (symmetrical or asymmetrical), amine, diamine, triamine, tetraamine, ether, diglyme, triglyme, tetraglyme, phosphine, carbonyl, dialkyl sulfide, vinyltrimethylsilane, and allyltrimethylsilane,

or

Lewis base stabilized Ir(I) β -ketoiminates of formula II:



10

wherein R, R', and R'' are the same or different, and are independently selected from the group consisting of H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base, preferably selected from the group consisting of alkene, diene, cycloalkene, cyclodiene, cyclooctatetraene, alkyne, substituted alkyne (symmetrical or asymmetrical), amine, diamine, triamine, tetraamine, ether, diglyme, triglyme, tetraglyme, phosphine, carbonyl, dialkyl sulfide, vinyltrimethylsilane, and allyltrimethylsilane.

20

For the Lewis base in the above precursors of formulae I and II, one or more Lewis base molecules may be preferred, especially for ether, alkene, alkyne, carbonyl and phosphine ligands. In some embodiments of precursors of formula

II, R and R' may be identical and R'' will be independently selected from the substituents listed above.

In CVD-based embodiments of the present invention, either a bubbler or organic
5 solution liquid delivery can be utilized for the chemical vapor deposition of the
Ir/IrO₂ thin film. The specific precursor may be suitably optimized for the
delivery and transport of the precursor to the CVD reactor. The precursor is
decomposed in the presence of an oxidant (e.g., O₂, O₃, or N₂O) to preferentially
deposit the metal Ir (< 500 °C) or the oxide, IrO₂ (>550 °C). In some
10 applications, the formation of a bi-layered Ir/IrO₂ film may be preferred.

The etching of Ir and IrO₂ in the practice of the invention, after the initial
formation of the iridium-containing film, may be carried out with the use of
halogen-based systems, such as chlorine, bromine, and fluorine based plasma or
15 ion beam etch chemistries. The formation of halogens of Ir(I) and Ir(III) can be
exploited to etch and pattern electrodes for semiconductor and ferroelectric device
applications. In systems where IrO₂ is present, the use of either a reducing pre-
treatment (to return the iridium oxide to Ir metal) or the use of fluorine etchants
may be preferred. The formation and removal of etch by-products depends on the
20 volatility of the halide species. The addition of stabilizing co-reactants may
usefully be employed to facilitate the removal and etching of the materials.

The iridium-containing films deposited in accordance with the method of the
present invention may be etched with a dry etch method, as more fully described
25 in the aforementioned co-pending U.S. Patent Application No. 08/966,796,
optionally using specific chemical enhancements to the rate of etching. The
addition of carbon monoxide, trifluorophosphine, or trialkyl phosphines can

accelerate the rate of etching by enhancing the volatility of the produced etch by-products.

For example, in the etching of the Ir-containing film on the substrate, the removal
5 rate for the process may be advantageously accelerated by the presence of carbon monoxide (CO). The rates are strongly dependent upon the gas-phase partial pressure of the reactants in elevated substrate temperature regimes (e.g., 725 - 975 °C). The presence of CO may serve to enhance the reactant volatility through the formation of $(\text{CO})_y\text{IrX}_3$ (where $\text{X} = \text{Cl}, \text{Br}$) and for $\text{Ir}(\text{Cl})_4$. IrF_6 may also be
10 employed for such purpose. These materials can be used advantageously for etching Ir in halogen-based plasmas, ion beams and in hybrid etching schemes.

In some instances, it may be desirable to convert the iridium oxide material deposited on the substrate to a pure iridium metal for a specific fabrication or
15 device application. In such instance, the deposited film of iridium oxide may be exposed to a reducing gas, such as hydrogen, forming gas, CO, ROH, etc. to effect such conversion.

After its formation and any additional patterning, the iridium-containing electrode
20 may have deposited thereon a high temperature dielectric and/or ferroelectric material in the same oxidizing ambient environment employed for the deposition of the iridium-containing film.

It is therefore unnecessary to purge the chamber of a reducing atmosphere, or to
25 transfer the substrate article bearing the iridium-containing film from the iridium deposition chamber to a dielectric/ferroelectric deposition chamber, as has been done in the prior art to accommodate the usage of hydrogen or other reducing gas

(forming gas) atmospheres in the iridium electrode formation step. The method of the invention therefore achieves a substantial simplification of the procedure for forming a capacitor or other microelectronic device in which the iridium-containing electrode is overcoated with a dielectric or ferroelectric material.

5

The iridium films deposited in the practice of the present invention may therefore be utilized for the formation of electrode and other elements of semiconductor devices, such as for example DRAMs, FRAMs, hybrid systems, smart cards and communication systems, as well as any other applications in which the thin films of iridium and/or iridium oxide are advantageously employed, such as catalytic systems.

10

Industrial Applicability

15 The invention provides iridium-containing precursors and a method for forming an iridium-containing film on a substrate using such precursors. The precursors and method of the invention may be employed to deposit an iridium film on a substrate. The deposited iridium film may be etched for patterning an electrode of a microelectronic device structure, e.g., a thin film capacitor, for fabrication of semiconductor devices in applications such as DRAMs, FeRAMs, hybrid systems, smart cards and communication systems.

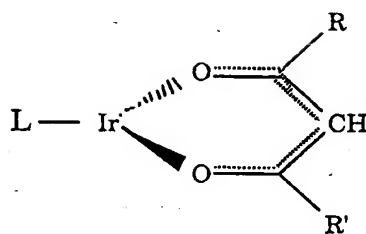
20

THE CLAIMS

1. A method of forming an iridium-containing film on a substrate, from an iridium-containing precursor thereof which is decomposable to deposit iridium on
5 the substrate, said method comprising decomposing the precursor and depositing iridium on the substrate in an oxidizing ambient environment.
2. A method according to claim 1, wherein the oxidizing ambient environment comprises an atmosphere containing an oxidizing gas selected from
10 the group consisting of oxygen, ozone, air, and nitrogen oxide.
3. A method according to claim 1, wherein the iridium deposited on the substrate comprises elemental iridium.
- 15 4. A method according to claim 1, wherein the iridium deposited on the substrate comprises iridium oxide, or a combination of iridium and iridium oxide.
5. A method according to claim 1, wherein the precursor comprises a
20 composition selected from the group consisting of:

Lewis base stabilized Ir(I) β -diketonates of formula I:

13

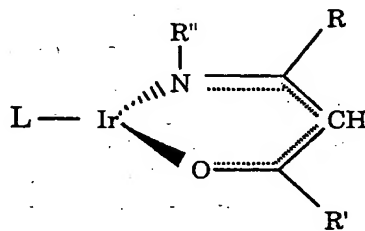


I

wherein R and R' may be alike or different and may be H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base; and

5

Lewis base stabilized Ir(I) β-ketoiminates of formula II:



II

10

wherein R, R', and R'' are the same or different, and are independently selected from the group consisting of H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base.

15

6. A method according to claim 5, wherein the coordinating Lewis base is selected from the group consisting of alkene, diene, cycloalkene, cycloalkadiene, cyclooctatetraene, alkyne, substituted alkyne (symmetrical or asymmetrical),

amine, diamine, triamine, tetraamine, ether, diglyme, triglyme, tetraglyme, phosphine, carbonyl, dialkyl sulfide, vinyltrimethylsilane, and allyltrimethylsilane.

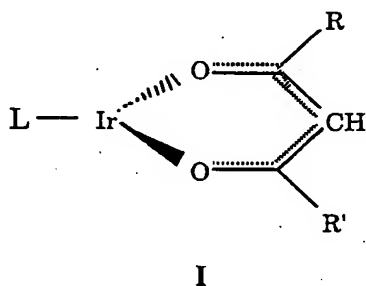
7. A method according to claim 1, wherein the oxidizing ambient
5 environment comprises air.

8. A method according to claim 1, wherein the decomposition of the
precursor and deposition of iridium on the substrate is carried out by a process
selected from the group consisting of chemical vapor deposition (CVD), assisted-
10 CVD, ion plating, rapid thermal processing, and molecular beam epitaxy.

9. A method according to claim 1, wherein the precursor comprises a
composition selected from the group consisting of:

15

Lewis base stabilized Ir(I) β -diketonates of formula I:



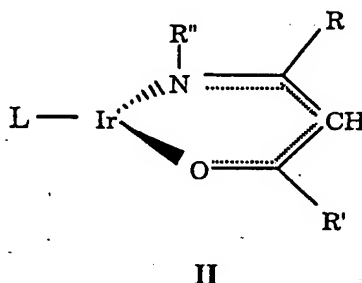
20

wherein R and R' may be alike or different and may be H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base.

10. A method according to claim 9, wherein the coordinating Lewis base is selected from the group consisting of alkene, diene, cycloalkene, cyclodiene, cyclooctatetraene, alkyne, substituted alkyne (symmetrical or asymmetrical), amine, diamine, triamine, tetraamine, ether, diglyme, triglyme, tetraglyme, 5 phosphine, carbonyl, dialkyl sulfide, vinyltrimethylsilane, and allyltrimethylsilane.

11. A method according to claim 1, wherein the precursor comprises a composition selected from the group consisting of:

10 Lewis base stabilized Ir(I) β -ketoiminates of formula II:



wherein R, R', and R'' are the same or different, and are independently selected from the group consisting of H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ 15 perfluoroalkyl, and L is a coordinating Lewis base.

12. A method according to claim 11, wherein the coordinating Lewis base is selected from the group consisting of alkene, diene, cycloalkene, cyclodiene, 20 cyclooctatetraene, alkyne, substituted alkyne (symmetrical or asymmetrical), amine, diamine, triamine, tetraamine, ether, diglyme, triglyme, tetraglyme, phosphine, carbonyl, dialkyl sulfide, vinyltrimethylsilane, and allyltrimethylsilane.

13. A method according to claim 1, wherein the decomposition of the precursor and deposition of iridium on the substrate is carried out by chemical vapor deposition.
- 5 14. A method according to claim 1, wherein the iridium deposited on the substrate is processed to yield an iridium-containing film element on the substrate, having critical dimensional characteristics below about 0.5 micron.
- 10 15. A method according to claim 14, wherein the decomposition of the precursor and deposition of iridium on the substrate is carried out by chemical vapor deposition.
- 15 16. A method of forming a microelectronic device or precursor structure on a substrate, including an electrode operatively associated with a high-temperature dielectric or ferroelectric material deposited thereover, said method comprising:
- (A) forming an iridium-containing film on the substrate, from an iridium-containing precursor thereof which is decomposable to deposit iridium on the substrate, comprising:
- 20 (i) decomposing the precursor and depositing iridium on the substrate in an oxidizing ambient environment; and
- (ii) processing the deposited iridium into an iridium-based
- 25 electrode element; and

(B) depositing on the iridium-based electrode element a high temperature dielectric and/or ferroelectric material.

17. A method according to claim 16, wherein the iridium-based
5 electrode element has deposited thereon a high temperature dielectric material.

18. A method according to claim 16, wherein the iridium-based
electrode element has deposited thereon a high temperature ferroelectric material
selected from the group consisting of SBT and PZT.

10

19. A method according to claim 16, wherein the microelectronic
device or precursor structure comprises a DRAM or FRAM capacitor device or
structure.

15

20. A method according to claim 16, wherein the high temperature
dielectric and/or ferroelectric material comprises a material selected from the
group consisting of SBT, PZT, BST, PLZT, PNZT, and LaCaMnO_3 .

20

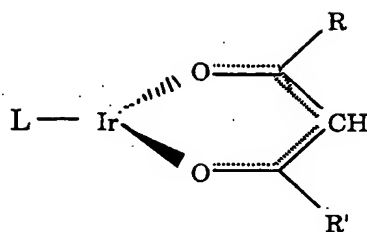
21. A method according to claim 16, wherein the iridium deposited on
the substrate comprises elemental iridium.

25

22. A method according to claim 16, wherein the iridium deposited on
the substrate comprises iridium oxide or a combination of iridium and iridium
oxide.

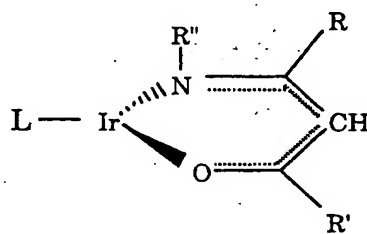
23. A method according to claim 16, wherein the precursor comprises
a composition selected from the group consisting of:

Lewis base stabilized Ir(I) β -diketonates of formula I:



wherein R and R' may be alike or different and may be H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base; and

Lewis base stabilized Ir(I) β -ketoiminates of formula II:



wherein R, R', and R'' are the same or different, and are independently selected from the group consisting of H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base.

24. A method according to claim 23, wherein the coordinating Lewis base is selected from the group consisting of alkene, diene, cycloalkene, cyclodiene, cyclooctatetraene, alkyne, substituted alkyne (symmetrical or asymmetrical), amine, diamine, triamine, tetraamine, ether, diglyme, triglyme, 5 tetraglyme, phosphine, carbonyl, dialkyl sulfide, vinyltrimethylsilane, and allyltrimethylsilane.

25. A method according to claim 23, wherein the oxidizing ambient environment comprises air.

10

26. A method according to claim 16, wherein steps (A)(i), (A)(ii) and (B) are carried out in the same oxidizing ambient environment.

27. A microelectronic device structure comprising an iridium oxide 15 electrode element formed in an oxidizing ambient environment and overlaid by a high temperature dielectric, wherein the electrode is conductively operative in relation to the high temperature dielectric.

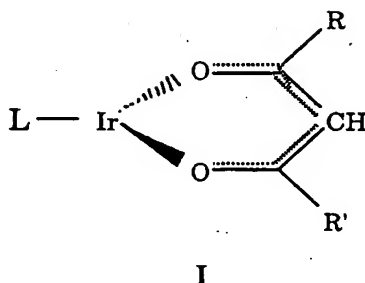
28. A microelectronic device structure according to claim 27, wherein 20 the high temperature dielectric comprises a material selected from the group consisting of SBT, PZT, BST, PLZT, PNZT, and LaCaMnO_3 .

29. A microelectronic device structure according to claim 27, wherein the high temperature dielectric comprises SBT.

25

30. A composition selected from the group consisting of:

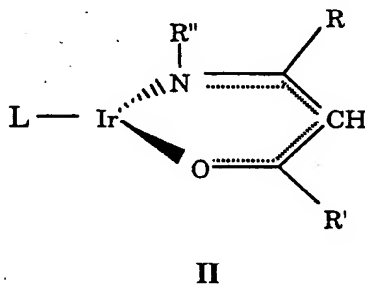
Lewis base stabilized Ir(I) β -diketonates of formula I:



5

wherein R and R' may be alike or different and may be H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base; and

10 Lewis base stabilized Ir(I) β -ketoiminates of formula II:



15

wherein R, R', and R'' are the same or different, and are independently selected from the group consisting of H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base.

20

31. A method according to claim 30, wherein the coordinating Lewis base is selected from the group consisting of alkene, diene, cycloalkene,

cyclodiene, cyclooctatetraene, alkyne, substituted alkyne (symmetrical or asymmetrical), amine, diamine, triamine, tetraamine, ether, diglyme, triglyme, tetraglyme, phosphine, carbonyl, dialkyl sulfide, vinyltrimethylsilane, and allyltrimethylsilane.

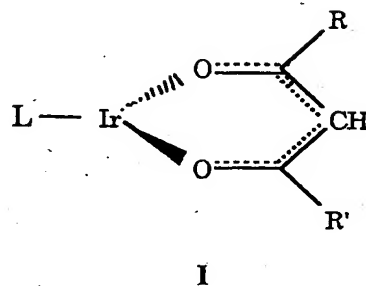
AMENDED CLAIMS

[received by the International Bureau on 12 April 1999 (12.04.99);
original claims 1, 30 and 31 amended; new claims 32-45 added;
remaining claims unchanged (6 pages)]

1. A method of forming an iridium-containing film on a substrate, from an iridium-containing precursor thereof which is decomposable to deposit iridium on the substrate, said method comprising liquid source delivery of said precursor, decomposing the precursor and depositing iridium on the substrate in an oxidizing ambient environment.
2. A method according to claim 1, wherein the oxidizing ambient environment comprises an atmosphere containing an oxidizing gas selected from the group consisting of oxygen, ozone, air, and nitrogen oxide.
3. A method according to claim 1, wherein the iridium deposited on the substrate comprises elemental iridium.
4. A method according to claim 1, wherein the iridium deposited on the substrate comprises iridium oxide, or a combination of iridium and iridium oxide.
5. A method according to claim 1, wherein the precursor comprises a composition selected from the group consisting of:

Lewis base stabilized Ir(I) β -diketonates of formula I:

Lewis base stabilized Ir(I) β -diketonates of formula I:

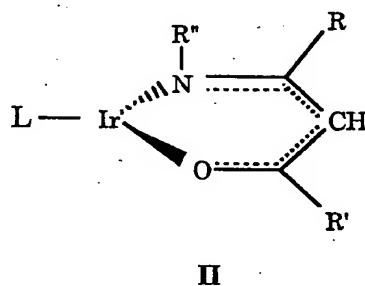


5

wherein R and R' may be alike or different and may be H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base; with the provisos that L is not carbonyl, L is not a cyclodiene, and L does not contain phosphine; and

10

Lewis base stabilized Ir(I) β -ketoiminates of formula II:



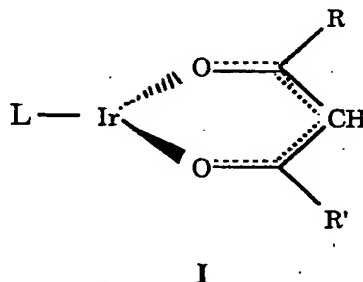
15

wherein R, R', and R'' are the same or different, and are independently selected from the group consisting of H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base.

20

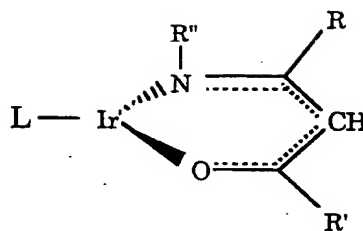
31. A composition according to claim 30, wherein the coordinating Lewis base is selected from the group consisting of alkene, diene, cycloalkene, cyclooctatetraene, alkyne, substituted alkyne (symmetrical or asymmetrical), amine, diamine, triamine, tetraamine, ether, diglyme, triglyme, tetraglyme, dialkyl sulfide, vinyltrimethylsilane, and allyltrimethylsilane.

32. A Lewis base stabilized Ir(I) β -diketonate of formula I:



- wherein R and R' may be alike or different and may be H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base selected from the group consisting of alkene, diene, cycloalkene, cyclooctatetraene, alkyne, substituted alkyne (symmetrical or asymmetrical), amine, diamine, triamine, tetraamine, ether, diglyme, triglyme, tetraglyme, dialkyl sulfide, vinyltrimethylsilane, and allyltrimethylsilane.

33. A Lewis base stabilized Ir(I) β -ketoiminate of formula II:



II

wherein R, R', and R'' are the same or different, and are independently selected from the group consisting of H, aryl, perfluoroaryl, C₁ - C₆ alkyl, or C₁ - C₆ perfluoroalkyl, and L is a coordinating Lewis base.

34. A composition according to claim 33, wherein the coordinating Lewis base is selected from the group consisting of alkene, diene, cycloalkene, cyclodiene, cyclooctatetraene, alkyne, substituted alkyne (symmetrical or asymmetrical), amine, diamine, triamine, tetraamine, ether, diglyme, triglyme, tetraglyme, phosphine, carbonyl, dialkyl sulfide, vinyltrimethylsilane, and allyltrimethylsilane.

35. A method according to claim 1, wherein the iridium-containing precursor comprises an iridium (I) precursor.

36. A method according to claim 1, wherein the iridium-containing precursor is selected from the group consisting of Lewis base-stabilized Ir(I) β -diketonates and Lewis base-stabilized Ir(I) β -ketoiminates.

37. A method according to claim 1, wherein the iridium-containing precursor is selected from the group consisting of Lewis base-stabilized Ir(I) β -diketonates, wherein the Lewis base is not carbonyl, a cyclodiene or a phosphine.

38. A method of forming an iridium-containing film on a substrate, from an iridium(I)-containing precursor thereof which is decomposable to deposit iridium on the substrate, said method comprising decomposing the precursor and depositing iridium on the substrate in an oxidizing ambient environment.

39. A method according to claim 38, wherein the iridium-containing precursor is selected from the group consisting of Lewis base-stabilized Ir(I) β -diketonates and Lewis base-stabilized Ir(I) β -ketoiminates.

15

40. A method according to claim 39, wherein when the precursor is a Lewis base-stabilized Ir(I) β -diketonate, the Lewis base is not carbonyl, a cyclodiene or a phosphine.

20

41. A method according to claim 39, wherein the Lewis base is selected from the group consisting of alkene, diene, cycloalkene, cyclooctatetraene, alkyne, substituted alkyne (symmetrical or asymmetrical), amine, diamine, triamine, tetraamine, ether, diglyme, triglyme, tetraglyme, dialkyl sulfide, vinyltrimethylsilane, and allyltrimethylsilane.

25

42. A method according to claim 38, comprising liquid delivery MOCVD for decomposing the precursor and depositing iridium on the substrate.

43. A method according to claim 38, wherein the precursor is decomposed in the presence of an oxidant selected from the group consisting of oxygen, ozone and N_2O to deposit iridium metal or iridium oxide.

44. A method according to claim 43, wherein iridium metal is deposited at a temperature below 500 degrees Centigrade.

45. A method according to claim 43, wherein iridium oxide is deposited at a temperature above 550 degrees Centigrade.

STATEMENT UNDER ARTICLE 19

Please replace original page 12 of the application as originally filed with the enclosed new replacement page 12.

enclosed new replacement pages 20, 21A, 21B, 21C, and 21D.

In the enclosed substitute pages 12 and 20-21D, the method and composition of applicant's invention have been claimed in a manner more specifically reciting the liquid source delivery of the precursor in claim 1, and more specifically claiming the precursor composition in claims 30-45.

It therefore is requested that the International Preliminary Examination of this application proceed on the basis of the claims 1-45 now pending in the application.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/23791**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C23C 16/18; C07F 15/00

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/226, 229, 255.3; 438/381, 681, 686; 556/9, 13, 16, 136, 137; 257/71

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS; STN**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 08-260148 A (FUJITSU LTD) 8 October 1996, col. 2, lines 10-20, col. 6, lines 30-50, Figure 7.	1-31
X	Database CAPLUS on STN, American Chemical Society (Washington, DC, USA) Accession No. 1983:63195, BROUWERS et al., 'Photochemistry of acetylacetonato-, trifluoroacetylacetonato-, and hexafluoroacetylacetonatodicarbonylrhodium and -iridium complexes in frozen gas mixtures at 12 K', abstract, University of Amsterdam, September, 1982.	30, 31
X	HITCHCOCK et al., Fluorophosphine Complexes of Rhodium(I) and Iridium(I). J. Chem. Soc. Dalton Trans. July, 1985, pages 1295-1301, especially page 1297.	30, 31

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

27 JANUARY 1999

Date of mailing of the international search report

12 FEB 1999

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

TIMOTHY MEERS

Telephone No. (703) 308-0664

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/23791

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X - A	GERFIN et al., Groth of Iridium Films by metal organic Chemical Vapor Deposition, Thin Solid Films, April, 1994, pages 352-355.	30, 31 ---- 1-15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/23791

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

427/226, 229, 255.3; 438/381, 681, 686; 556/9, 13, 16, 136, 137; 257/71